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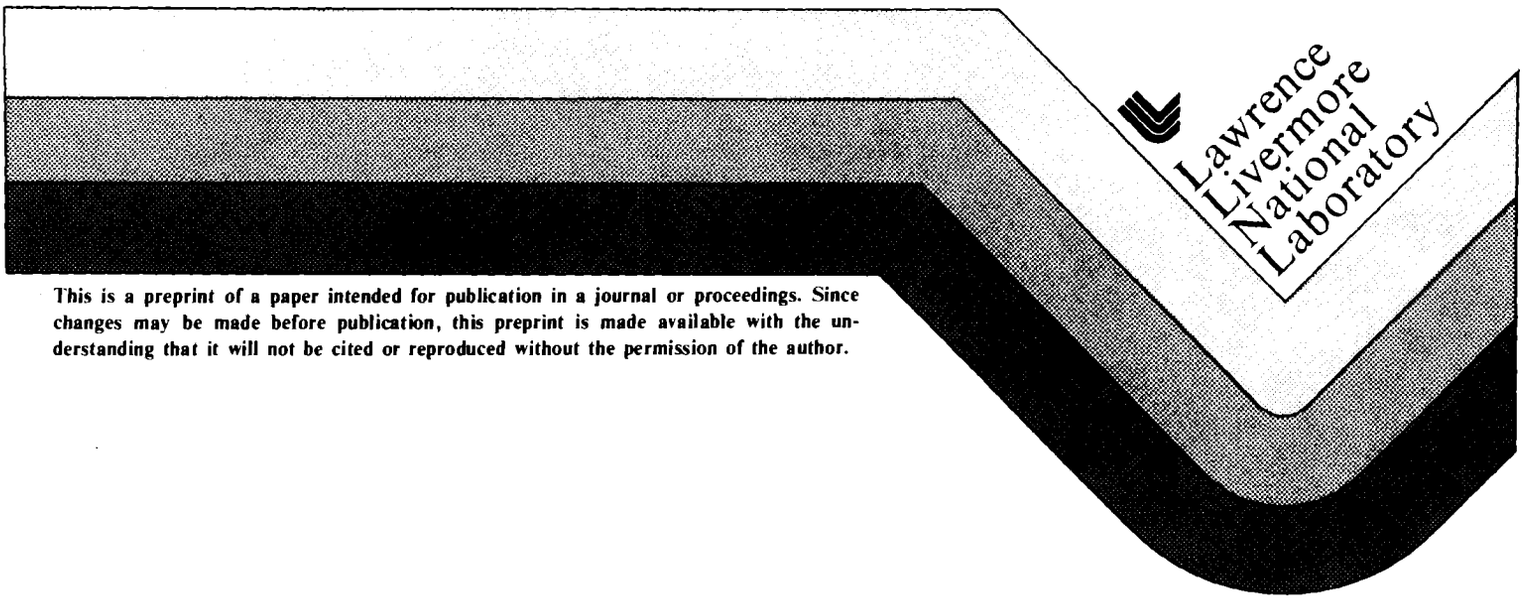

DISCLAIMER

THE INFLUENCE OF DILUENTS AND INHIBITORS ON DETONATIONS

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ABSTRACT

The present paper reports on a series of experiments performed to determine the influence of chemical inhibitors and diluents on the detonability of fuel-air and fuel-oxygen mixtures. The influence of adding small amounts (1-3%) of CF_3Br, CF_4 and CO_2 to ethylene-air mixtures was determined by performing large scale critical tube diameter tests. The results of these tests show that the inhibition effect of CF_3Br on detonations is not nearly as dramatic as it is on flames. For detonations, the relatively chemically inert diluent CO_2 is found to be a better inhibitor than CF_3Br. Similar laboratory test with ethylene-oxygen and hydrogen-oxygen mixtures confirm the results obtained for fuel-air mixtures. In fact, the addition of small amounts of CF_3Br to these fuel-oxygen mixtures has a small sensitizing effect, whereas the influence of CO_2 is similar to that observed for fuel-air mixtures. The results are compared with the prediction of a detailed chemical kinetic model for the oxidation and inhibition processes. For CF_3Br, it is found that a chemical kinetic scheme derived from flame data predicts a detonation inhibiting effect much larger than that observed. Possible modifications of this scheme to obtain a consistent description of CF_3Br inhibition are proposed and discussed.

1. INTRODUCTION

Inhibition and extinction of hydrocarbon flames by additives are practical problems which have been investigated for a number of years. Flame inhibitors and suppressants are usually characterized by their reduction in burning velocity and by the amount required to extinguish the flame. An important class of chemical inhibitors are the halogenated compounds or Halons. These inhibitors interfere with the chemical reactions within the combustion zone, so that small amounts can produce dramatic inhibition effects. It has been observed, for example, that CF_3Br (Halon 1301) is about five times as effective as CO_2, on a volumetric basis, in reducing the laminar burning velocity of methane-air mixtures[1] and in extinguishing laminar methane-air flames[2]. However, the effectiveness of Halons in suppressing more violent explosions has not been clarified. Hertzberg[3] has reported that the effect of added CF_3Br on stoichiometric methane-air explosions depends on the ignition energy. Furthermore, the inhibition appears to be effective only in the initial stages of confined explosions. According to Hertzberg et al.[4], once the confined explosion has developed beyond the initial stages the inhibitor is rendered ineffective either by the compression process or by the onset of turbulent propagation. It has therefore not been demonstrated that halogenated compounds are effective for mitigation of the more severe explosions hazards involving turbulent flame acceleration, confined explosions and transition to detonation.

The potentially most destructive explosions are those involving detonation. The detonation hazards of an explosive mixture can be characterized by the critical energy, E_c, required to initiate detonation in the mixture and the critical tube diameter, d_c, required for a detonation emerging from a tube to transmit to an unconfined detonation. Matsui and Lee[5] have proposed that either E_c or d_c can be used to assess the relative sensitivity of explosive mixtures to detonation. Both the critical initiation energy and the critical tube diameter depend on the nature of the cellular detonation structure and on the detailed chemical kinetic processes within the cellular detonation front. Chemical additives, such as halogenated species, interfere with these chemical kinetic processes and would therefore be expected to affect both the detonability properties and the cellular structure of detonations.

The addition of halogenated species has been shown to increase significantly the chemical induction time in some fuel-oxygen mixtures[6]. In general, longer induction times correspond to less detonable mixtures. Thus, if similar increases also occur for practical fuel-air mixtures, halogenated species could have an important role in reducing the detonation hazards of these mixtures.

A few experiments have been reported in which the influence of chemical inhibitors on detonations have been determined. In particular, Libouton et al.[7] have shown that the addition of small amounts (2%) of CF_3Br to $CO/H_2/O_2/Ar$ mixtures increases the detonation cell size by about a factor of two. For $H_2/O_2/Ar$ mixtures, however, the addition of CF_3Br suppresses the regularity of the cellular structure without modifying the cell size very much. This latter result is consistent with the observation of Macek[8] that the addition of CF_3Br to H_2/O_2 mixtures has a slight sensitizing effect on the initiation of detonation. The critical initiation energy (E_c) is reduced from 10.5 Joules to 8.3 Joules when 2% CF_3Br is added to the H_2/O_2 mixture. For fuel-air mixtures the situation is even more unclear. The only experimental result which has been reported is the observation by Bull[9] that addition of CF_3Br to methane-air appears to have a sensitizing rather than an inhibiting effect. Numerical calculations based on detailed chemical kinetic schemes for hydrocarbon oxidation[10] and for inhibition by halogenated species[11] have been performed for selected fuel-air mixtures. These calculations predict a fairly dramatic inhibiting effect. With only 1% CF_3Br added to a ethylene-air mixture, for example, the characteristic reaction zone length was predicted to increase by more than a factor of two. The numerical predictions are sensitive to the chemical kinetic rates which are used for the individual reactions. In many cases these are not well known, so that selected experimental results are required in order to validate or to determine the limitations of the chemical kinetic scheme.

The present paper reports on an investigation of the influence of chemical inhibitors and diluents on the critical tube diameter for ethylene-air mixtures, and for hydrogen- and ethylene- oxygen mixtures. The investigations

were focussed on the influence of the common halogenated inhibitor CF_3Br (Halon 1301) and the relatively inert additive CO_2. Selected results for other additives are also reported. Correlations of the experimental results using a modified chemical kinetic scheme are described. In addition, the purely thermal effects of the added compounds on the detonation sensitivity are calculated.

2. EXPERIMENTAL DETAILS

a) Large Scale Field Tests

The experimental test facility at DRES has been described in detail elsewhere [12,13]. The facility is centered around an 18.3 m x 7.6 m concrete test pad onto which the experimental apparatus can be mounted. A sketch of the configuration used in the present tests is shown in Fig. 1a. The test section consists of a 0.89 m diameter steel tube, 8 m long, connected to a 1.78 m diameter plastic bag, 3.4-5 m long, constructed from 0.13 mm thick polyethylene.

The test fuel (CP grade, 99.5% pure ethylene) was first mixed with the initial air in the test volume by a multi-path recirculation system using a high-capacity centrifugal blower. The composition and mixture homogeniety in the test volume were verified by continuously analyzing samples from two ports in the test section using a "Wilks Miran 80" infrared gas analyzer. This system was adequate to guarantee the fuel concentration and fuel-air homogeniety in the test volume to within ±0.05% fuel. Once the desired fuel-air concentration had been achieved, a precalibrated volume of halogenated compounds (CF_3Br or CF_4) or CO_2, contained in one or two high pressure bottles, was added to the test section. The main uncertainty in additive concentration is due to uncertainty in the volume of the test section. This uncertainty is less than 10%. Homogeniety of the resulting mixture was achieved by recirculating the mixture at least five times through the system prior to initiation of detonation by a slug of acetylene-oxygen at one end of the tube.

The progress of the detonation and the detonation pressure profiles were monitored at up to seven positions along the tube-bag configuration using piezoelectric pressure transducers. Cinematographic records of the diffraction

of the detonation wave from the tube were obtained using a "Hycam" camera (~12,000 half fps) looking normal to the direction of propagation. Smoked foils, consisting of polished steel sheets covered with a thin layer of carbon soot, were mounted in the tube near the exit to the bag to record the detonation structure.

b) Laboratory Tests

The laboratory tests were performed in a detonation tubes opening up into a larger detonation chamber simulating an unconfined environment. A sketch of the configurations used in the present experiments is shown in Fig 1b. The 25 mm and 40 mm diameter tubes were used to determine the influence of small amounts (5%) of halogenated compounds (CH_3Br, CH_3Cl and CF_3Br), as well as CO_2, on the critical initial pressure for successful transmission of detonations in stoichiometric H_2/O_2 mixtures from the tube into the larger chamber. The influence of 5% CF_3Br on the transmission properties of detonations in C_2H_4/O_2 mixtures of equivalence ratios 0.8, 1.0 and 1.5 was determined using the 50 mm diameter tube.

All mixtures were prepared by the method of partial pressures. Spark or exploding wire ignition along with a Shchelkhin spiral was used to ensure consistent detonation initiation. The dignostics in the tube consisted of two ion probes and one piezoelectric pressure transducer to monitor the detonation velocity and pressure. The detonation cellular structure was also recorded in selected tests by placing a smoked foil near the exit end of the tube. Success or failure of detonation transmission was determined by monitoring the velocity between the pressure transducer near the exit to the detonation chamber and a piezoelectric pressure transducer mounted on the end wall of the detonation chamber.

3. MODELS AND CORRELATIONS

One of the aims of the experimental investigation was to provide critical tests for a chemical kinetic model which has been proposed for the inhibition of detonation by halogenated additives. This model, which has been described in detail elsewhere [10,11] makes use of the one-dimensional Zeldovich-

von Neumann-Döring model of the detonation wave in order to calculate the relative detonation length scales (i.e., the critical tube diameter d_c; the cell width S; and the critical explosion length $(E_c/p_0)^{1/3}$, where E_c is the critical initiation energy and p_0 the initial pressure) with and without additives. An induction length characteristic of the explosive mixture is given by $\Delta = \tau u$, where τ is the chemical induction time behind the shock wave propagating at C-J velocity and u is the post-shock particle velocity relative to the shock front. The detonation length scales are then assumed to be proportional to this induction zone length. The induction time τ, defined as the time of maximum rate of temperature increase, is calculated using detailed models of the chemical reaction mechanisms behind the shock wave. Extensive calculations on the chemical kinetics of gaseous detonations have been performed using this approach[10,14,15]. By adding the chemical processes describing the reactions of the additive molecules, the induction zone length with additives can also be calculated. A detailed chemical kinetic model describing the inhibition of hydrocarbon oxidation by halogenated compounds has previously been used to predict the variation in induction zone length for ethylene-air when small amounts of these compounds are added to the mixture[11]. In this paper, the same reaction scheme is used to calculate the induction zone length without additives (Δ_0) and with additives (Δ) at a given fuel-oxidizer equivalence ratio. The ratio of detonation length scales with and without inhibitor is then assumed to be equal to Δ/Δ_0 at that equivalence ratio. This is similar to the approach used by Lee et al.[16] to calculate the variation of detonation cell size for hydrogen-air with added CO_2.

The most extensive chemical kinetic calculations are performed for ethylene-air, and for ethylene and hydrogen in oxygen, with added CF_3Br and CO_2. In addition, calculations are performed for the $CO/H_2/O_2/Ar$ system with added CF_3Br investigated by Libouton et al.[7]. The chemical kinetic reaction schemes proposed in Refs. 10, 11, 14 and 15 are used for these calculations. However, it was found necessary to adjust some of the inhibition reaction rates for CF_3Br in order to obtain agreement with the present experimental results. This adjustment will be described in the next section.

The change in detonation sensitivity when compounds are added to fuel-oxidizer mixtures is due to a combination of chemical and thermal effects. The thermal effects are caused by changes in C-J velocity and post-shock thermodynamic conditions. Depending on the thermodynamic properties of the additive, the thermal effects alone can lead to significant changes in detonation sensitivity. The change in thermodynamic conditions can be obtained by including the additive in standard equilibrium C-J and shock calculations[17]. The length scale corresponding to these modified conditions can then be calculated using a global induction length formula for the length scale without additives.

Global induction length formula for many fuel-air systems have been reported by Moen et al.[18]. They have correlated the length scale data by using an induction length formula of the form;

$$L = uk\ [\text{Fuel}]^a\ [\text{Oxygen}]^b \exp(E_a/RT), \qquad (1)$$

where L is the critical tube diameter, cell size or the critical explosion length, and u, [Fuel], [Oxygen] and T are the post-shock relative particle velocity (m/s), fuel and oxygen concentrations (moles/liter), and temperature (K) behind a shock wave propagating at the C-J detonation velocity of the explosive mixture. The relevant correlation parameters for ethylene and hydrogen in air are given in Table I. These correlation parameters are used to calculate the purely thermal effect of additives on the detonation sensitivity of these mixtures.

4. RESULTS

a) Fuel-air Mixtures

The critical tube diameter results for the ethylene-air system with added CF_3Br, CF_4 and CO_2 are summarized in Fig. 2. The uncertainity in ϕ for each mixture represents Go and No-Go results for the 0.89 m diameter tube. These results should be compared with the reference curve, which represents a correlation of critical tube diameter results with no additives[18]. The results with added CF_3Br show that the dramatic inhibiting effect predicted by

Westbrook[11] is not observed. In fact, the inhibiting effect of CF_3Br on ethylene-air detonations is less than that of CO_2. The relative inhibiting effects for detonations are therefore quite different than for laminar flames, where CF_3Br is found to be five times as effective as CO_2[1,2].

Although the inhibition effects of CF_3Br are not as dramatic as predicted, there is some inhibition. This inhibition must be due to chemical interference with the oxidation process since, as shown in Fig. 2, a purely thermal calculation predicts a sensitizing effect. A sensitivity analysis of the inhibitor mechanism proposed in Ref. 11, varying only the reaction rates involving the inhibitor chemistry, shows that only one reaction has a dramatic effect on the overall induction length. This reaction is:

$$CF_3Br + H = CF_3 + HBr. \qquad (2)$$

The predictions by Westbrook[11] shown in Fig. 2 are based on the rate for this reaction obtained by Biordi et al.[19] from flame data. In order to obtain reasonable agreement with the present experimental results, this rate must be decreased by a factor of ten. The revised predictions for 3% CF_3Br, with this decreased rate, are also shown in Fig. 2.

The Go-NoGo results with 1.5% CF_4 are consistent with no effect at all, in agreement with the observations of Libouton et al.[7] for the $CO/H_2/O_2/Ar$ and $H_2/O_2/Ar$ systems. Any inhibiting influence of CF_4 must be chemical in nature, since purely thermal effects result in a slight decrease in the critical tube diameter (i.e., a sensitizing influence).

Of the three additives tested, CO_2 is the most effective in reducing the detonation hazards of ethylene-air. The addition of 3% CO_2 increase the critical tube diameter by about 1.5, corresponding to an increase in the critical initiation energy by a factor of about $(1.5)^3 \simeq 3.4$. Similar inhibition of hydrogen-air mixtures by CO_2 were obtained by Lee et al.[16]. The influence of added 3% CO_2 on lean ethylene-air mixtures is correctly predicted by either the chemical kinetic model or from thermal effects along, indicating that CO_2 is a relatively chemically inert additive whose effect on the detonation sensitivity can be estimated from thermodynamic considerations.

b) Fuel-Oxygen Mixtures

The relative influence of CF_3Br and CO_2 on the detonation sensitivity is even more dramatic for fuel-oxygen mixtures. The experimental results which are summarized in Fig. 3 show that the addition of 5% CF_3Br to stoichiometric H_2/O_2, and stoichiometric and lean C_2H_4/O_2, actually reduces the critical initial pressure for transmission from tubes. In other words, CF_3Br acts as a sensitizer rather than an inhibitor for these mixtures. This is consistent with the observation by Macek[8] that the critical initiation energy for H_2/O_2 is reduced when small amounts of CF_3Br is added. The effect of added CO_2 is similar to that for fuel-air mixtures. The critical tube diameter increases by 30-50% when 5% CO_2 is added.

The curves shown in Fig. 3 are obtained from the detailed chemical kinetic model of the oxidation and inhibition processes. By normalizing at one experimental point for each fuel-oxygen mixture without additive, the variation of the critical tube diameter with initial pressure and with additives is predicted. As can be seen in Fig. 3a, the predicted variation with initial pressure is in good agreement with the experimental results of Matsui and Lee[5]. The observed inhibiting effect of CO_2 is also correctly reproduced for stoichiometic C_2H_4/O_2. However, for H_2/O_2 the effect of CO_2 is underestimated.

For ethylene-air mixtures, it was necessary to reduce the rate for the reaction $CF_3Br + H = CF_3 + HBr$ by a factor of ten in order to account for the observed effect of CF_3Br. The same reduction in rate is also necessary to account for the observed sensitizing effect of CF_3Br on H_2/O_2 and C_2H_4/O_2 mixtures. With the original rate, an inhibiting effect on H_2/O_2 and C_2H_4/O_2 is predicted by the chemical kinetic model. The curves shown in Fig. 3 for 5% CF_3Br, which were obtained with the reduced rate, account quite well for the observed sensitizing effect on H_2/O_2 and C_2H_4/O_2. However, the model fails to account for the small inhibition observed for rich C_2H_4/O_2. This is further illustrated in Fig. 4, where the variation in critical pressure for a 50 mm tube is plotted vs. C_2H_4/O_2 equivalence ratio with no additives and with 5% CF_3Br. Notice that the added CF_3Br changes from a sensitizer at stoichiometric composition to a slight inhibitor at an equivalence ratio of 1.5. Both the

chemical kinetic model and a thermal effects model predict a sensitizing effect for all of these C_2H_4/O_2 compositions. The thermal effects model is based on the induction length correlation for ethylene-air with an activation energy of 37.2 kcal/mole. A different activation energy would change the effect. However, the temperature behind the C-J shock increases when CF_3Br is added so that a sensitizing influence is obtained for all activation energies.

Based on the chemical kinetic model, the influence of CF_3Br on acetylene/oxygen and ethane/oxygen is predicted to be similar that for C_2H_4/O_2. However, a fairly dramatic inhibition effect is predicted for methane/oxygen mixtures. With 5% CF_3Br, the critical tube diameter for methane/oxygen is predicted to increase by a factor of 2.1.

In addition to CF_3Br and CO_2, the influence of CH_3Br and CH_3Cl on stoichiometric H_2/O_2 detonations was determined by monitoring the critical initial pressure for transmission from a 40 mm tube. The results are shown in Table II. Of the four added compounds, CO_2 is by far the most effective inhibitor for this mixture. The order of inhibition effectiveness by the halogenated compounds is exactly the reverse of that predicted in Ref. 11 based on chemical kinetic considerations. A better understanding of the inhibition/sensitizing mechanisms of these compounds on detonations is clearly required. One aspect, which the chemical kinetic model cannot account for is the increased irregularity of the cellular structure observed when these compounds are added to the H_2/O_2 mixture. It may, in fact, be necessary to take this increased irregularity into account in order to describe the inhibition/sensitizing mechanisms. The possible role of the cellular structure on these mechanisms will be discussed further in the next section.

5. DISCUSSION

The present results clearly show that CF_3Br is not nearly as effective an inhibitor for detonations as it is for laminar flames. In fact, for all the mixtures tested CO_2 is a much better detonation inhibitor. The dramatic inhibition of detonations predicted based on inhibition rates derived from flame data is not observed. A reduction by a factor of ten in the rate for

$CF_3Br + H = CF_3 + HBr$ is required in order to obtain reasonable agreement with the present fuel-air or fuel-oxygen results. A possible reason for the lower rate could be the neglect of the importance of the reaction with the methyl radicals ($CF_3Br + CH_3 = CF_3 + CH_3Br$) by Biordi et al.[19] in their flame analysis. They would therefore arrive at too large a rate for the reaction of H atoms with CF_3Br. It is also important to note that the flame results with added CF_3Br reported in Ref. 11 and 20 were not affected by reducing the rate for $CF_3Br + H = CF_3 + HBr$ by a factor of ten. A relatively consistent description of CF_3Br inhibition of hydrocarbon oxidation can therefore be achieved with this reduced rate.

Unfortunately, the reduced rate does not agree with either the detonation or flame results for the $CO/H_2/O_2/Ar$ system investigated by Libouton et al.[7] and Safieh et al.[21]. The latter authors obtain approximately the same rate as Biordi et al.[18] for the reaction of H with CF_3Br from flame analysis of this system which does not involve the methyl radical (CH_3). Furthermore, the increase in cell size with added CF_3Br observed by Libouton et al.[7] is consistent with the original rate. No influence of CF_3Br is obtained with the reduced rate.

The main differences between the hydrocarbon/oxygen systems and the $CO/H_2/O_2/Ar$ system are the concentrations of H,O,OH and CH_3 during the induction period. Thus, if the failure of the chemical kinetic model is due the chemical inhibition scheme, the proposed reactions involving these radicals with CF_3Br are likely responsible for the failure. Note that no reactions with O or OH are included in the proposed scheme[11,20]. Possible modifications of the inhibition scheme to account for the observed discrepancies are now being studied. The results of this study will be included in the final paper.

An alternate explanation for the failure of the chemical kinetic model could be related to the simplifying assumption that the physical detonation length scales are linearly related to the induction zone length calculated at C-J conditions from a one-dimensional model of the detonation. Chemical kinetic models based on this assumption have been relatively successful in correlating detonation length scales for sensitive mixtures [10,14,15]. However, these

correlations fail to account for the behavior of less sensitive fuel-air mixtures[12]. It has been suggested that this failure is related to increased irregularity of the cellular structure for fuel-air mixtures[18]. The cellular structure of detonations also degenerates when small amounts of CF_3Br are added. This increased irregularity could account for the failure of the chemical kinetic model to consistently describe the effect of adding CF_3Br. It may therefore be necessary to include at least some aspects of the coupling between chemistry and gasdynamics within the cellular detonation front. In other words, a detailed model of the chemical processses is not sufficient, the influence of these processes on the structure of the detonation must also be taken into account in order to properly describe the influence of chemical additives on detonations. Such considerations are outside the scope of the present paper.

7. CONCLUSION

The results from the large scale critical tube diameter tests show that the common halogenated flame inhibitor CF_3Br is not as effective as CO_2 in reducing the detonation hazards of ethylene-air mixtures. These results are supported by similar results obtained with fuel-oxygen mixtures. For the latter mixtures, CF_3Br acts as a detonation sensitizer rather than an inhibitor.

From a practical point of view, these results show that the effectiveness of chemical inhibitors depends on the nature of the combustion proccesses. Results obtained for laminar flames do not necessarily apply to other types of explosions. It is therefore important to first identify the type of explosion hazard, and then to test the effectiveness of various inhibitors for this type explosion hazard before choosing a fire or explosion suppressant.

Chemical kinetic models of the inhibition processes can be useful tools for predicting the effectiveness of different chemical additives. However, selected experimental results are required to validate the inhibition schemes. The present results show that the inhibition of detonations by CF_3Br predicted from a simplified one-dimensional model of the detonation, using a chemical kinetic model of the inhibition processes derived from flame data, is not

observed. A relatively consistent scheme of CF_3Br inhibition of hydrocarbon flames and detonations can be obtained by reducing the rate for the process $CF_3Br + H = CF_3 + HBr$. However, this reduced rate does not agree with detonation or flame results for the $CO/H_2/O_2/Ar$ system with added CF_3Br. Further modifications of the inhibition scheme are therefore required in order to obtain a consistent description of all available experimental results. It is also possible that the failure of the chemical kinetic model is not due to the chemistry of the inhibition but to the simple one-dimensional model which is used to relate the chemistry to the detonation properties.

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REFERENCES

1. Strasser, A., Liebman, I. and Kuchta, J. M.: Fire Technology 10, 25 (1974).

2. Sorenson, S. C., Savage, L. D. and Strehlow, R. A.: Combustion and Flame 24, 347 (1975).

3. Hertzberg, M.: "Fuel-Air Explosions" (J. H. Lee and C. Guirao, Eds.), SM Study No. 16, p. 3, University of Waterloo Press, 1982.

4. Hertzberg, M., Johnson, A. L., Kuchta, J. M. and Furno, A. L.: Sixteenth Symposium (International) on Combustion, p. 767, The Combustion Institute, 1977.

5. Matsui, H. and Lee, J. H.: Seventeenth Symposium (International) on Combustion, p. 1269, The Combustion Institute, 1979.

6. Skinner, G. B.: "Halogenated Fire Suppressants", (R. G. Gann, Ed.), ACS Symposium Series No. 16, p. 295, American Chemical Society, 1975.

7. Libouton, J. C., Dormal, M. and van Tiggelen, P. J.: Fifteenth Symposium (International) on Combustion, p. 79, The Combustion Institute, 1975.

8. Macek, A.: AIAA Journal 1, 1915 (1963).

9. Bull, D. C.: "Fuel-Air Explosions", (J. H. Lee and C. Guirao Eds.), SM Study No. 16, p. 139, University of Waterloo Press, 1982.

10. Westbrook, C. K.: Combustion and Flame 46, 191 (1982).

11. Westbrook, C. K.: Nineteenth Symposium (International) on Combustion, p. 127, The Combustion Institute, 1982.

12. Moen, I. O., Murray, S. B., Bjerketvedt, D., Rinnan, A., Knystautas, R. and Lee, J. H. S.: Nineteenth Symposium (International) on Combustion, p. 635, The Combustion Institute, 1982.

13. Funk, J. W., Murray, S. B., Moen I. O. and Ward, S. A.: "Fuel-Air Explosions", (J. H. Lee and C. Guirao, Eds.), SM Study No. 16, p. 565, University of Waterloo Press, 1982.

14. Westbrook, C. K.: "Fuel-Air Explosion", (J. H. Lee and C. Guirao, Eds.), SM Study No. 16, p. 189, University of Waterloo Press, 1982.

15. Westbrook, C. K. and Urtiew, P. A.: Nineteenth Symposium (International) on Combustion, p. 615, The Combustion Institute, 1982.

16. Lee, J. H. S., Knystautas, R., Guirao, C., Benedick, W. B. and Shepherd, J. E.: "Hydrogen-Air Detonations", Presented at the Second International Workshop on the Impact of Hydrogen on Water Reactor Safety, Albuquerque, New Mexico, October 3-7, 1982.

17. Gordon, S. and McBride, B.: "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks, and Chapman-Jouguet Detonations", NASA Report SP-273, Washington, D. C., 1976.

18. Moen, I. O., Thibault, P. A., Funk, J. W., Ward, S. A. and Rude, G. M.: "Detonation Length Scales for Fuel-Air Explosives", Proceedings of the 9th International Colloquium on Dynamics of Explosions and Reactive Systems, Poitiers France, July 3-8, 1983, Prog. Astronaut. Aeronaut, (in press).

19. Biordi, J. C., Lazzara, C. P. and Papp, J. F.: J. Phys. Chem. 81, 1139, (1977).

20. Westbrook, C. K.: Comb. Science and Technology 34, 201 (1983).

21. Safieh, H. Y., Vandooren, J. and van Tiggelen, P. J.: Nineteenth Symposium (International) on Combustion, p. 117, The Combustion Institute (1982).

FIGURE CAPTIONS

Figure 1 a) Sketch of the large scale experimental configuration.
b) Sketch of the laboratory experimental configurations. The dimensions of the different configurations are given in the table inset.

Figure 2 Critical tube diameter for ethylene-air with additives. (% additive refers to % of total mixture).

Figure 3 Critical tube diameter vs. initial pressure for H_2/O_2 and C_2H_4/O_2 mixtures with and without additives (% additive refers to % of total mixture). The curves are obtained from the chemical kinetic model. The results of Matsui and Lee (Ref. 5) are without additives.
a) Stoichiometric H_2/O_2 and C_2H_4/O_2
b) C_2H_4/O_2, ϕ = 0.8 and 1.5.

Figure 4 Critical initial pressure for transmission from a 50 mm diameter tube vs. C_2H_4/O_2 equivalence ratio. (The solid curves are drawn through the experimental results).

TABLE I

LENGTH SCALE CORRELATION FORMULAS

$L = uk\,[Fuel]^a\,[Oxygen]^b \exp(E_A/RT)$*

FUEL IN AIR	LENGTH SCALE	a,b	$k \times 10^{10}$	E_A (Kcal/mole)
ETHYLENE	CRITICAL TUBE	0, -1.0	5.65	37.2
HYDROGEN	CRITICAL TUBE	0, -1.0	5.58	31.7
	CELL WIDTH	0, -1.0	295	32.6

* UNITS: Concentrations, [Fuel] and [Oxygen], in moles/litre and velocity, u, in m/sec.

TABLE II

$2H_2 + O_2$ + ADDITIVE; TUBE DIAMETER 40 mm

ADDITIVE	CRITICAL INITIAL PRESSURE (torr)	LENGTH SCALE RATIO
0%	373 ± 17	1.0
5% CF_3Br	328 ± 28	0.8
5% CH_3Br	448 ± 33	1.14
5% CH_3Cl	483 ± 28	1.23
5% CO_2	595 ± 35	1.54

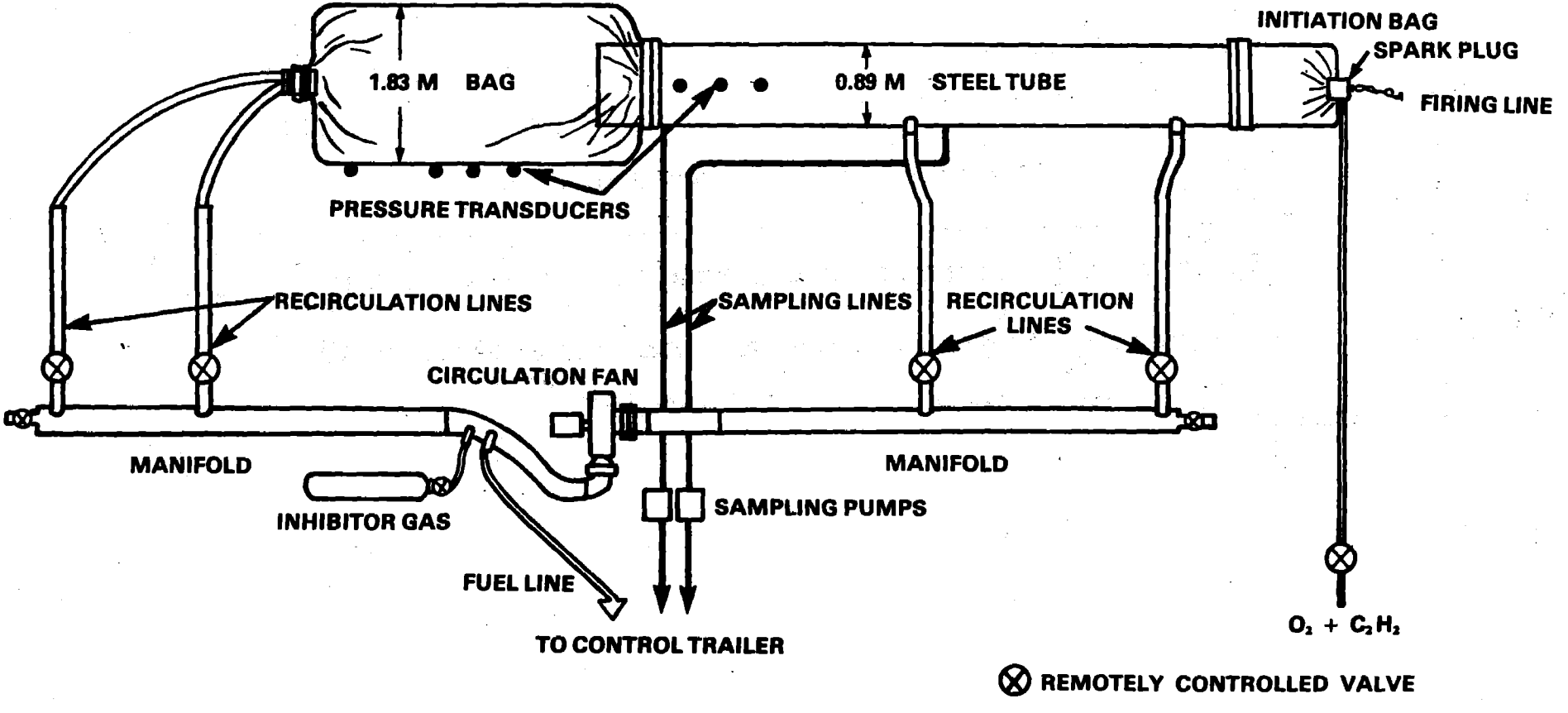
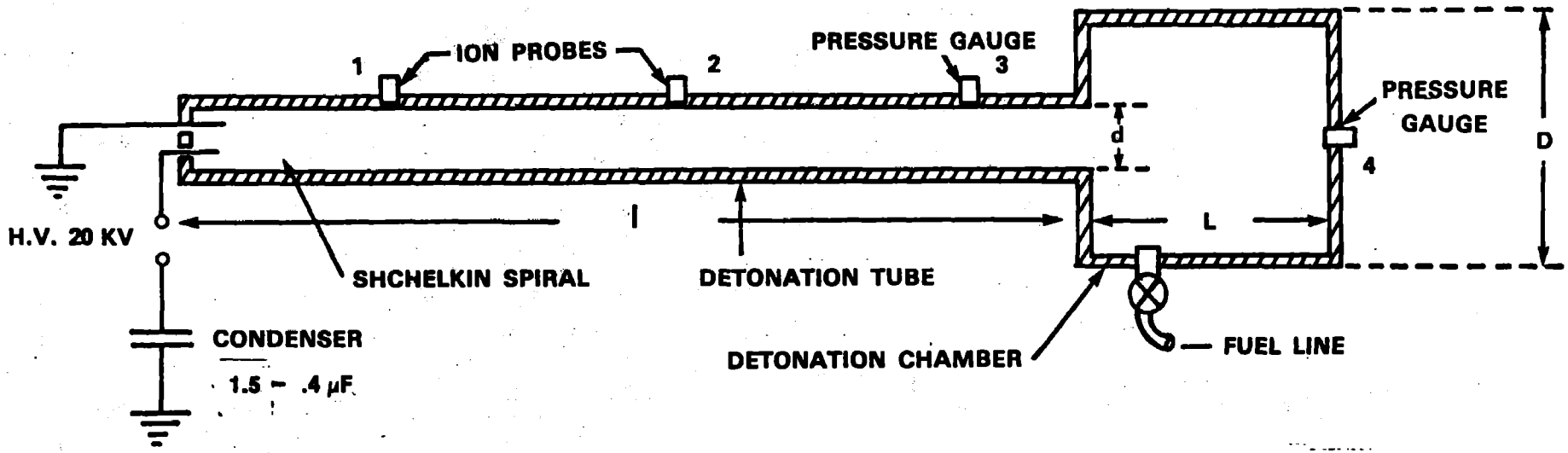
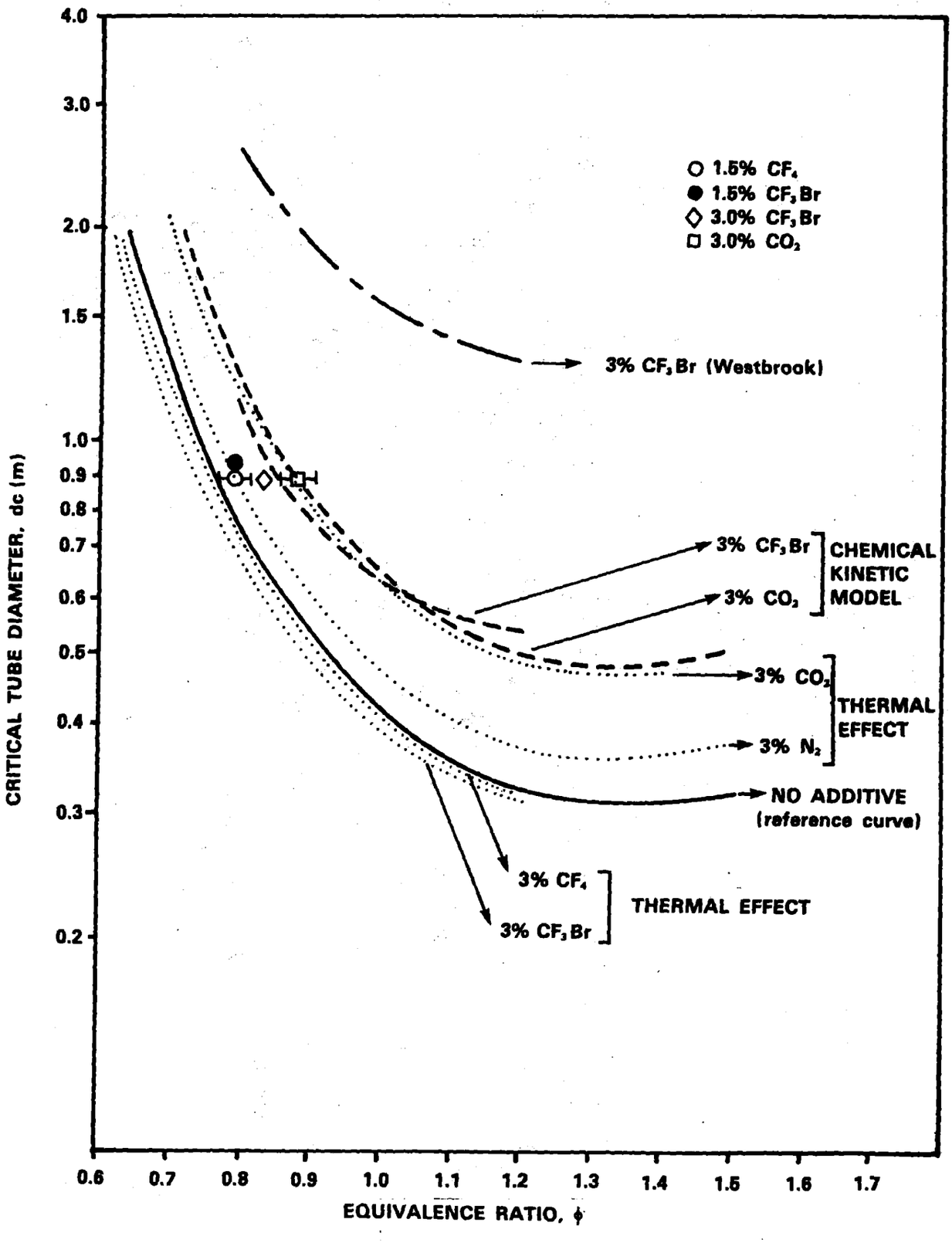

1.83 M BAG
0.89 M STEEL TUBE
INITIATION BAG
SPARK PLUG
FIRING LINE
PRESSURE TRANSDUCERS
RECIRCULATION LINES
SAMPLING LINES
RECIRCULATION LINES
CIRCULATION FAN
MANIFOLD
MANIFOLD
INHIBITOR GAS
SAMPLING PUMPS
FUEL LINE
TO CONTROL TRAILER
$O_2 + C_2H_2$
REMOTELY CONTROLLED VALVE

FIGURE 1a



d (mm)	l (mm)	D (mm)	L (mm)
25	1300	150	200
40	1300	150	200
50	1250	250	360

FIGURE 1b



Critical Tube Diameter for C_2H_4-Air-Additive

FIGURE 2

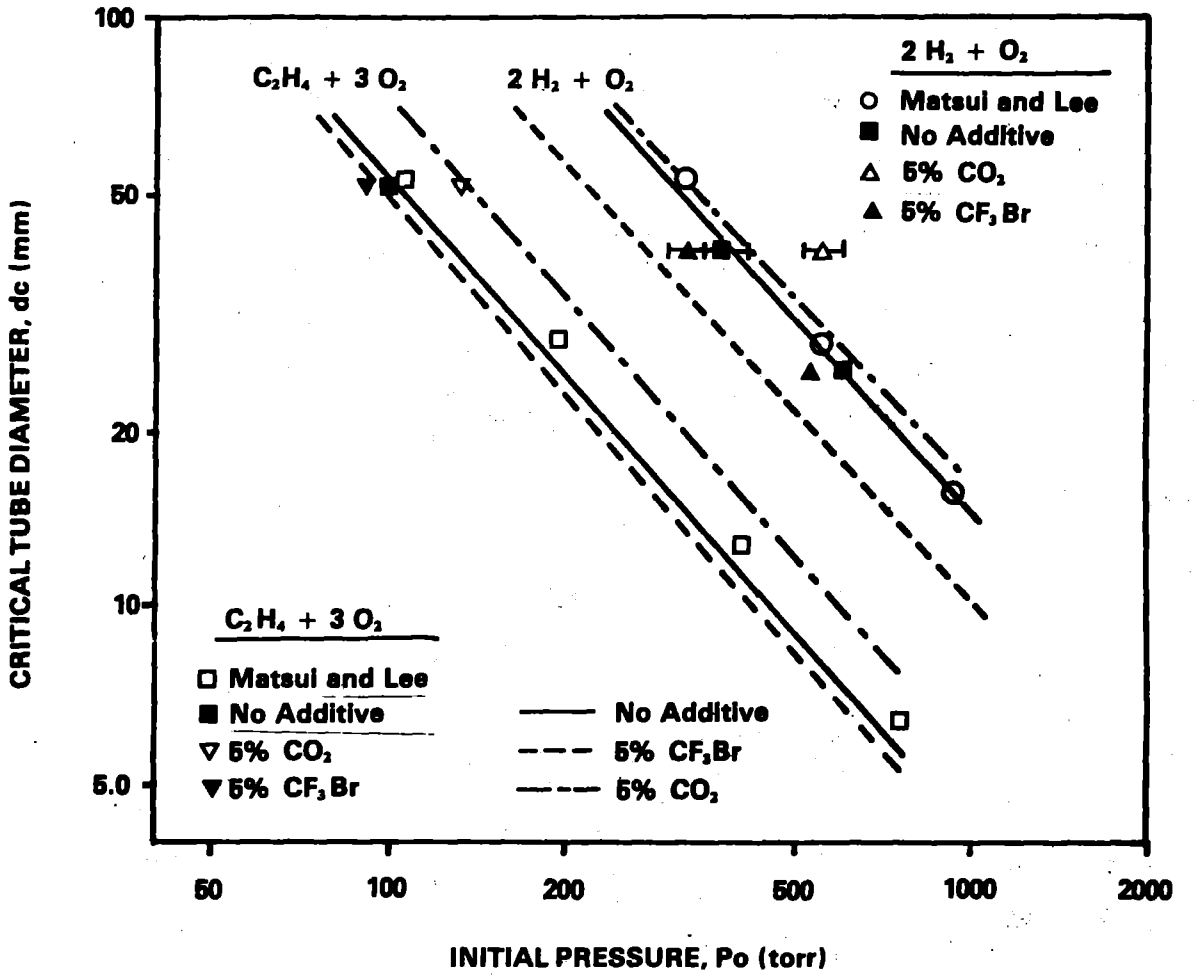

100
50
20
10
5.0
50
100
200
500
1000
2000
CRITICAL TUBE DIAMETER, dc (mm)
INITIAL PRESSURE, Po (torr)
C2H4 + 3 O2
2 H2 + O2
2 H2 + O2
Matsui and Lee
No Additive
5% CO2
5% CF3Br
C2H4 + 3 O2
Matsui and Lee
No Additive
5% CO2
5% CF3Br
No Additive
5% CF3Br
5% CO2

FIGURE 3a

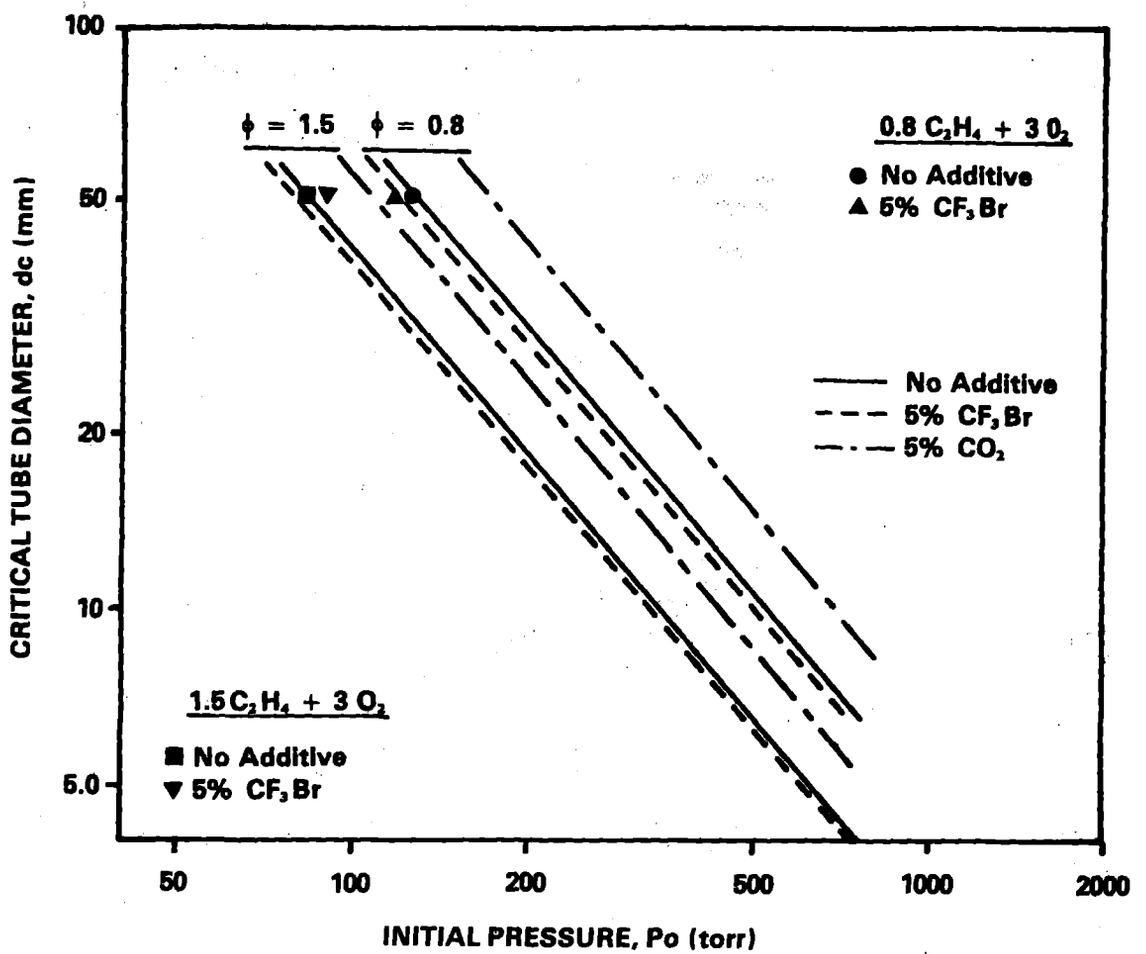

100
50
20
10
5.0
CRITICAL TUBE DIAMETER, dc (mm)
ϕ = 1.5
ϕ = 0.8
0.8 C2H4 + 3 O2
No Additive
5% CF3Br
No Additive
5% CF3Br
5% CO2
1.5 C2H4 + 3 O2
No Additive
5% CF3Br
50
100
200
500
1000
2000
INITIAL PRESSURE, Po (torr)

FIGURE 3b

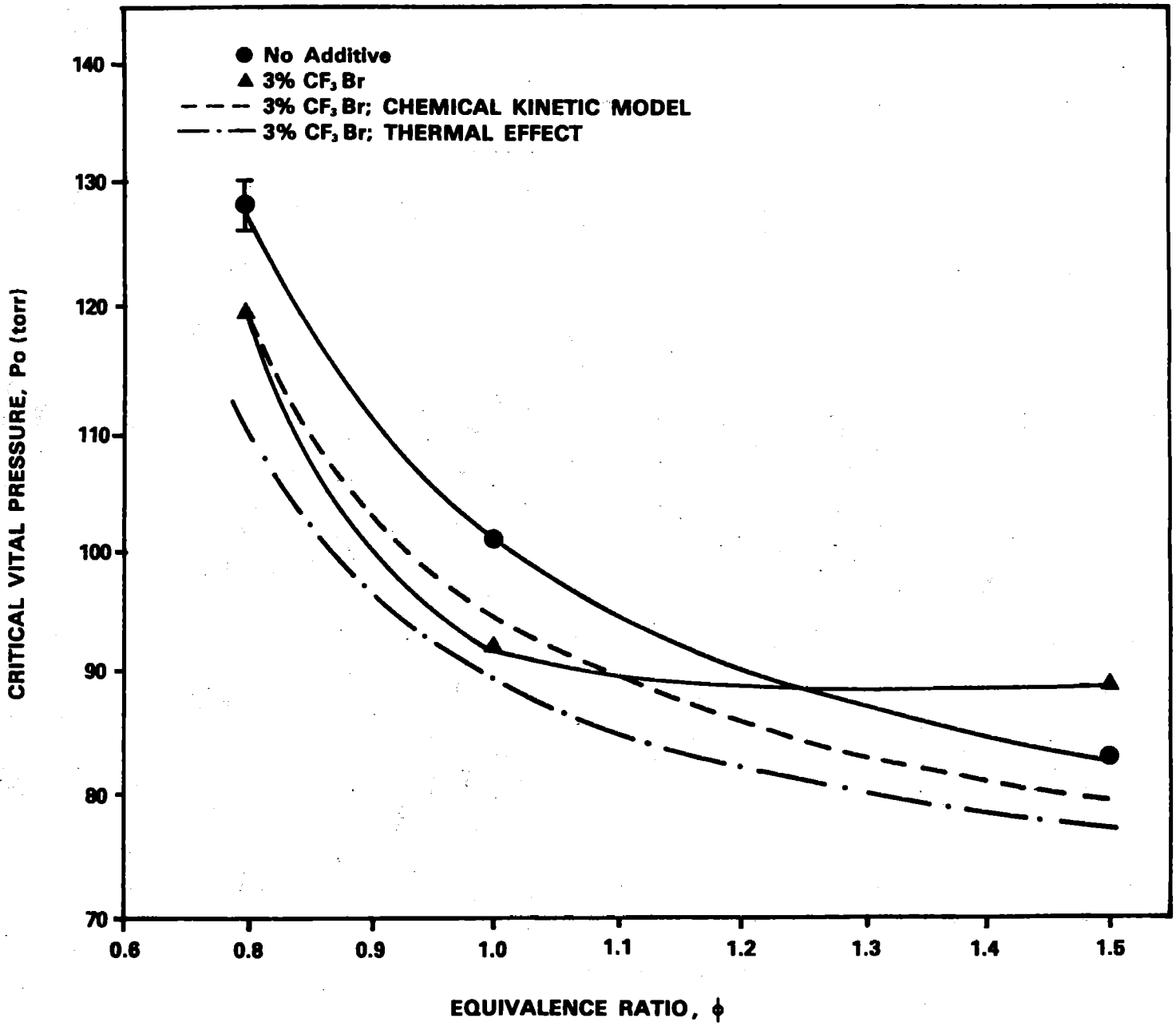

No Additive
3% CF_3Br
3% CF_3Br; CHEMICAL KINETIC MODEL
3% CF_3Br; THERMAL EFFECT
CRITICAL VITAL PRESSURE, Po (torr)
140
130
120
110
100
90
80
70
0.6
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
EQUIVALENCE RATIO, ϕ

FIGURE 4